# High pressure infrared studies of HMX

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## Abstract

We are studying the effects of pressure on HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) using infrared spectroscopy. The sample is put under pressure using a diamond anvil cell at ambient temperature, data is collected at the National Synchrotron Light Source in Brookhaven National Laboratory. In analyzing this data, we hope to learn more about the molecular vibrations as the molecule bends and deforms under pressure. Such understanding could aid in determining new safety standards or more efficient ways of using HMX. In future studies, we intend to include the aspect of temperature variation in addition to pressure, with the goal of describing the molecule in a phase diagram.
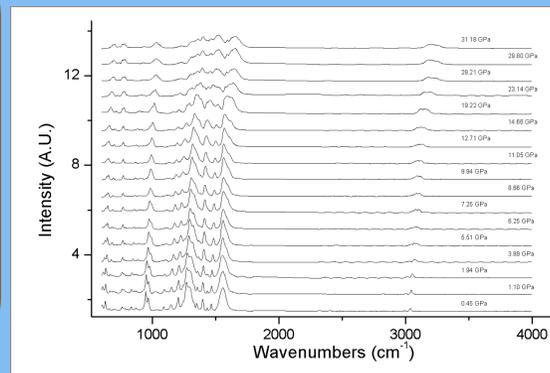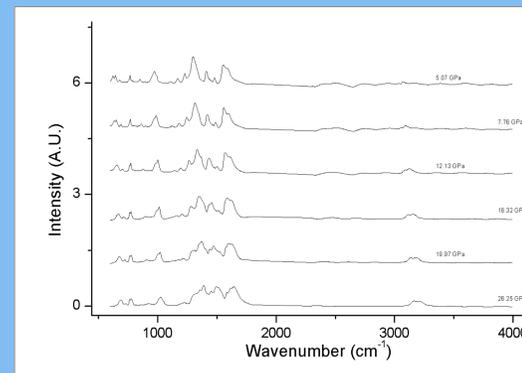
## Background

High pressure physics is used to study how materials change under pressure. One of the most common methods of obtaining high pressures in the gigapascal (GPa) range is the use of the diamond anvil cell (DAC.) A figure of a typical DAC is provided below.

HMX is used in a variety of applications, although it is almost exclusively used in military applications as a secondary explosive. As it is an insensitive explosive, it will not react under most normal conditions, even though it is one of the most powerful explosives manufactured today. Because of this, HMX is very easy to study, even when it is subjected to high pressure.

Ruby is used in most high pressure applications as a way of monitoring pressure. It is used as a well established method of monitoring pressure, as ruby florescence peaks are very sensitive to pressure changes.
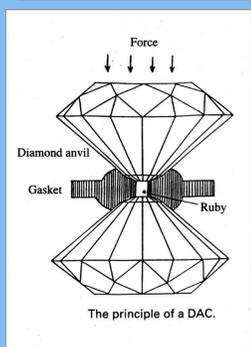


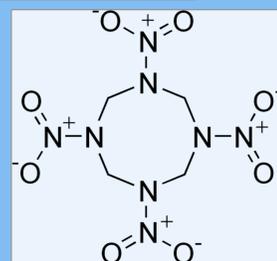Figure 1. Illustration of a diamond anvil cell (earth.northwestern.edu)



Figure 2. Molecular structure of HMX

## Experiment

We loaded HMX into a symmetric diamond anvil cell (DAC) at Brookhaven National Laboratory. We used KBr (Potassium Bromide) as a quasi-hydrostatic pressure transmitting medium, which is invisible in the infrared spectrum. Ruby powder was used to determine the current pressure of the sample. Half of the sample was pure KBr to be used for background subtraction, the second half was a thin layer of HMX with KBr on it. A Bruker Hyperion and Vertex 80V spectrometer was used to collect the infrared spectra of the HMX sample.
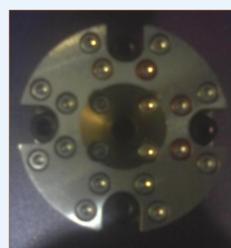


Figure 3. Symmetric DAC (top)



Figure 4. Symmetric DAC (side)

Data was collected at approximately 1.5 GPa intervals, up to a maximum of 30 GPa from ambient pressure. Ruby florescence was monitored using a 514 nm diode laser.

The collected data was then analyzed using OriginLab8 and CrystalSleuth. Each of the peaks was then matched to a database to determine which chemical bonds or vibrations it represents. This analysis is consolidated in a table to the right.



Graph 1. Infrared spectrum HMX compressed from 0.45 GPa to 31.18 GPa



Graph 2. Decompression of HMX, from high pressure (bottom) to low pressure (top)

## Analysis

Analysis of HMX major peaks at 0.45 GPa

| Peak Number | Theoretical (cm⁻¹) | Experimental (cm⁻¹) | Bond Type |
|---|---|---|---|
| 1 | 600 | 603 | Skeleton motion (whole ring vibration), ring vibration |
| 2 | 628 | 629 | $CH_2$ rk, $NO_2$ rk/sc |
| 3 | 660 | 660 | N-N str, $NO_2$ sc, CNC sc, $CH_2$ rk |
| 4 | 758 | 761 | $NO_2$ wg, N-N wg, CNC sc |
| 5 | 771 | 773 | $NO_2$ wg, N-N rk |
| 6 | 831 | 831 | CNC str, $NO_2$ str |
| 7 | 857 | 860 | CNC str, $NO_2$ str |
| 8 | 880 | 871 | N-N str, $NO_2$ sc, CNC str, $CH_2$ rk |
| 9 | 927 | 947 | N-N str, $CH_2$ rk, CNC str |
| 10 | 1066 | 1089 | $CH_2$ tw, $CH_2$ rk, N-N str (all bonds) |
| 11 | 1136 | 1147 | $CH_2$ rk (all bonds), N-N str (all bonds) |
| 12 | 1221 | 1205 | CH wg, N-N str, CNC asym str, CNC str, $NO_2$ str |
| 13 | 1250 | 1269 | CH wg, CNC asym str, $NO_2$ str |
| 14 | 1296 | 1290 | $CH_2$ wg, CH wg, $NO_2$ str, N-N str |
| 15 | 1315 | 1326 | $CH_2$ wg, $NO_2$ str, $CH_2$ sc, N-N str, CNC asym str |
| 16 | 1341 | 1350 | $CH_2$ tw, CNC asym str |
| 17 | 1363/1374 | 1396 | $CH_2$ sc, $CH_2$ wg |
| 18 | 1414 | 1433 | $CH_2$ sc |
| 19 | 1422 | 1467 | $CH_2$ sc |
| 20 | 1668 | 1556 | $NO_2$ asym str |
| 21 | 2990 | 2998 | $CH_2$ str |
| 22 | 3042/3053 | 3039 | $CH_2$ asym str |
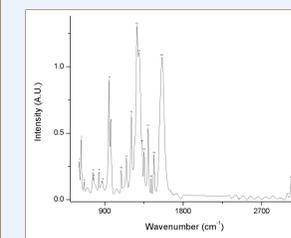


Figure 4. Infrared spectrum at 0.45 GPa

In analyzing the data obtained from each pressure, we are able to discern how certain peaks move or change with pressure, and how this may represent changes in the molecular structure. The above table compiles information for each of the major peaks and their corresponding bond types. Such tables were constructed for each pressure increase.

Each of the peaks are labeled according to their number on the graph to the left. These peaks change or disappear with increasing pressure, as shown in the waterfall plot, however in decompression, changes are reversed.

From this analysis we can determine no irreversible phase change as upon decompression the sample's spectrum returned to its ambient state.

## References

Reusch, William. "Infrared Spectroscopy." *Infrared Spectroscopy*. William Reusch, 10 Aug 2007. Web. 15 Jun 2010. <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm>.

Chickos, James, and David Garin. "Infrared Spectroscopy." *INTERACTIVE INSTRUCTIONAL TEXT*. UM-St. Louis Chemistry Department, 08 Dec 1997. Web. 28 Jul 2010. <http://www.umsl.edu/~orglab/documents/IR/IR2.html>.